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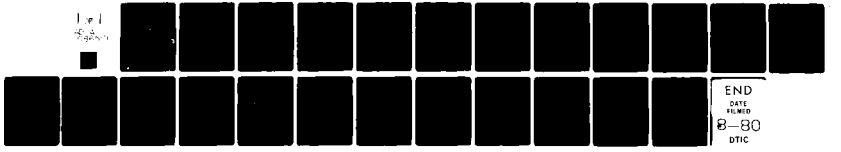

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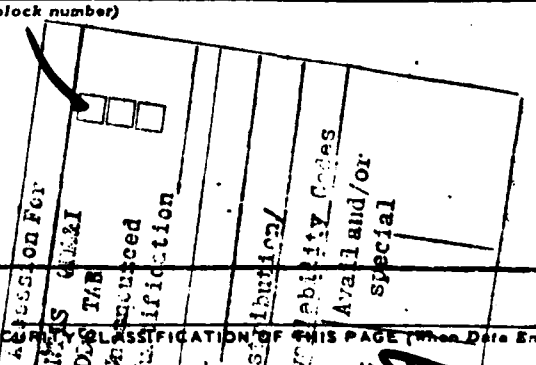

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CHEMISORPTION ON STEPPED SURFACES: O/STEPPED W(110)*

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In a previous study we have developed a general theory of chemisorption on certain stepped surfaces; namely those for which a lattice gas in thermodynamic equilibrium is an appropriate model. We showed there that a comparison of LEED (Low Energy Electron Diffraction) results for flat and stepped substrates can determine the change in adsorption energy at terrace edge sites. In the present work we demonstrate this via detailed Monte Carlo calculations for O on a certain stepped W(110) surface. We use oxygen adatom-adatom (AA) interaction energies previously determined by experimental and theoretical studies on flat W(110). By comparison with experimental results for the stepped surface system we find that the O binding energy is less strong at either terrace edge for this particular surface and defect.

I. Introduction

In a previous study[1] (referred to as I herein) we have presented a general theory of LEED scattering from overlayers on stepped surfaces, including the effects of statistical disorder in the overlayer. Systems that may be modeled by a lattice gas in thermal equilibrium were considered. We showed that the behavior of the LEED intensity as a function of coverage θ is strongly influenced by the sign of the change in adsorption energy at terrace edge sites. We also considered LEED spot splitting effects and pointed out that qualitatively new LEED features may arise at low (or high) θ values, due to differences in adatom-adatom (AA) interaction energies at terrace edge sites from their value elsewhere on the terrace.

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The present work applies the theory developed in I to existing experimental results[2] for O adsorbed on a certain stepped W(110) surface. In Section II we briefly review the theory presented in I. In Section III we describe the experimental data for O on stepped W(110). Integrated LEED intensity as a function of coverage θ and spot splitting results for the two adlayer domains are described. Section IV defines our theoretical model. A Monte Carlo program was employed to calculate the statistical averages of interest. As input we used AA energies for O/W(110) derived by comparison of experimental studies on the flat surface and theoretical lattice gas models. Section V contains the results of our calculations. Using the signs of the changes in adsorption energy at terrace edge sites as unknown parameters, we find that the observed LEED features are reproduced most accurately when the O adsorption is less strong at either terrace edge site than on the flat surface. Section VI contains some suggestions for future work. Perhaps most exciting is the prospect - already suggested by our results in I - that, very generally, one can determine the sign of the change in adsorption energy at terrace edge sites by a simple comparison of appropriate overlayer LEED results for the flat and stepped surfaces without detailed modeling.

II. Theory of LEED Scattering from Overlayers on Stepped Surfaces

In this section we review the main points of the theory developed in I. There we assumed the stepped surface was composed of identical terraces, with equivalent points on neighboring terraces separated by a fixed vector $\underline{g}$, and that N_s terraces were within the coherence length ξ of the LEED apparatus. We assumed the adatoms on a given terrace sit at N fixed sites $\underline{R}_\ell$, with occupation variable $n_\ell = 0(1)$ for an unoccupied (occupied) site. If the adatoms are in thermal equilibrium, and the AA forces of not too long range, it is reasonable to assume that the overlayer on each terrace is statistically independent of that on the others. Another important point is that for strong chemisorption the change

$\delta\varepsilon$ in adsorption energy at terrace edge sites will generally be such that $|\delta\varepsilon| >> kT$. Hence edge sites are either empty ($\delta\varepsilon > 0$) or occupied ($\delta\varepsilon < 0$) given a sufficient value of θ.

The result of all this was that in the kinematic (single-scattering) approximation the LEED intensity for scattering vector $\underline{k}$ is

$$I(\underline{k}) = N_s\left(\langle|p(\underline{k})|^2\rangle - |\langle p(\underline{k})\rangle|^2\right) + h(N_s, \underline{k}\cdot\underline{g})\,|\langle p(\underline{k})\rangle|^2 \qquad (1)$$

Here

$$p(\underline{k}) \equiv \sum_{\ell=1}^{N} \eta_\ell \exp(i\,\underline{k}\cdot\underline{R}_\ell)\,, \qquad (2)$$

$$h(N_s, x) \equiv \sin^2(N_s x/2) \,/\, \sin^2(x/2)\,. \qquad (3)$$

N is the number of adsorption sites on a terrace and the angular brackets denote a statistical average on a single terrace. The first term in Eq(1) includes effects of statistical disorder on a single terrace, while the second term includes effects of interterrace interference via the function h. Thus for a given stepped chemisorption system and set of LEED scattering parameters, the intensity I is determined by the termperature T, coverage θ, AA interactions, and signs of the changes $\delta\varepsilon$ in adsorption energy at terrace edge sites. All of these quantities except $\delta\varepsilon$ may be measured or determined by calculations for the corresponding flat surface adsorption system. Thus the sign of $\delta\varepsilon$ can be found by studying experimental results for the stepped surface. This is shown by means of a model calculation at T = 0 in I and also demonstrated with a (finite temperature) Monte Carlo calculation for O/stepped W(110) here.

In I we also consider several features of the LEED scattering in more detail. In particular, we show in a model calculation that the overlayer beam intensity $I(\underline{k}_0')$, where $\underline{k}_0'$ is an appropriately chosen scattering vector, has a maximum at a coverage θ_m that is characteristic of the change in adsorption energies $\delta\varepsilon$. This result is only due to the change in effective number of adsorption sites available on the stepped vs. flat surface. Thus one would expect a similar trend in the maximum of the integrated intensity $\bar{I}$ vs θ, where

$$\Phi \equiv \iint_{a} I(\underline{k}) \frac{d(\underline{k}\cdot\underline{a})}{2\pi} \frac{d(\underline{k}\cdot\underline{b})}{2\pi} \qquad (4)$$

In Eq(4), $\underline{a}$ and $\underline{b}$ are unit mesh vectors. Φ is an experimentally measurable quantity. The reciprocal space integration area a is determined by instrumental parameters and beam energy. This expectation is confirmed by the results in Section V.

In I we go on to consider the relative size of the contribution of $|\langle\rho\rangle|^2$ and $\langle|\rho|^2\rangle$ to Φ (these terms enter via the expression for I given in Eq(1)). We argue that the former often tends to be smaller. We also consider the splitting of LEED spots, which is due to interterrace interference via the function h in Eq(1). We show by means of general arguments and specific model calculations that the splitting strength depends on coverage, the signs of the $\delta\varepsilon$, and whether the terrace width is odd or even.

In what follows we consider the chemisorption systems O/W(110) and O on a certain stepped W(110) surface. We show that applying the general theory of I, described above, to experimental results for these systems leads to the conclusion that the O adsorption energy is less strong ($\delta\varepsilon>0$) for either terrace edge in this system. Similar information has been obtained[3] in field emission studies on other systems. There seems to be no general rule as to whether a given step is more or less adsorptive for a given adsorbate.

In applying our theory we make use of the AA interaction energies derived by Ching et al in a lattice gas treatment[4] of the flat surface chemisorption system. These parameters are employed as input in a statistical mechanical calculation of LEED scattering on the stepped surface chemisorption system with the $\delta\varepsilon$ as variables. The results of this calculation are compared with experiment. We find agreement only for $\delta\varepsilon>0$ on both terrace edges.

III. Experimental Results

The system O/W(110) has been extensively studied[5]. For $\theta < 0.5$, and $T<T_c(\theta)$ the adlayer shows (2x1) ordering. For $T > T_c$ it is in a disordered

state. The phase boundary T_c (θ) is observed to be approximately constant, $T_c \cong 450^oK$ for $.1 \leq \theta \lesssim 0.35$ and then jump abruptly to $T_c \cong 720^oK$ for $0.35 \lesssim \theta \leq .5$. AA (adatom-adatom) interaction energies have been derived by several authors[4] by comparing experimental and theoretical T_c results at a few θ values. We use the values determined by Ching et al which are illustrated in Fig. 1.

Note that in this system there are two degenerate (2X1) structures which are completely equivalent in the absence of defects. Hence the (1/2,1/2) and ($\overline{1/2}$,1/2) LEED beams have the same behavior as functions of θ and T.

An experiment for O on stepped W(110) has been performed by Engel et al.[2] The W crystals were cut so that the average terrace width D on one was D=10 adsorption sites and the other D=24. In the nomenclature of Lang et al.[6] these can be indexed as W-(S) [10(110)x(011)] and W-(S) [24(110)x(011)]. Thus the terrace edges are in the [$\overline{1}$10] direction, as illustrated in Fig. 2. This means that the two (2x1) overlayer domains become crystallographically inequivalent. Domain I refers to that with the [0,1] direction parallel to the terrace edge, domain II to the other, as shown in Fig. 2. The (1/2,1/2) (($\overline{1/2}$,1/2)) LEED beam corresponding to domain I(II) was monitored in this experiment.

In the calculations reported here, we considered the D=10 case only to minimize computer time. However the experimental results at D=24 are completely consistent with our interpretation. At D=10, experiments were done at three temperatures: $T=300^oK$, 460^oK and 1000^oK. We calculated at 460^oK only. There is evidence[7] that O diffusion rates on this surface fall considerably below 300^o, so that thermodynamic equilibrium may not be achieved. For $T \gtrsim 900^oK$ the steps on the clean surface begin to move[2]. (We note, however, that the results reported[2] for $T = 460^oK$ and 900^oK are in qualitative agreement with our interpretation.)

The experimental results[2] we will deal with include (a) the integrated LEED intensity and (b) the LEED overlayer spot shapes. Under (a) it was observed that while the integrated intensities I_I (for domain I) and I_{II} (for domain II) are roughly equal at low coverage ($\theta<0.1$), I_I is considerably larger than I_{II} for larger values of θ, as one would expect from the terrace orientation. Further, the maximum value of I_I is reached not at $\theta = 0.5$, which would correspond to a complete (2x1) overlayer on a flat surface, but at $\theta \cong 0.32$. (for D=24 the corresponding maximum is at $\theta \cong 0.44$). I_{II} has a minimum at a coverage slightly below the maximum in I_I in both cases. These results are illustrated in Fig. 3.

Under (b), the (1/2,1/2) (domain I) beam shows a splitting in the [$\bar{1}$ 1 2] direction at characteristic energies, from which terrace width and step heights were deduced. Also a minimum in intensity at the normal position of the (1/2,1/2) reflex was seen. The ($\overline{1/2}$,1/2) beam (domain II) showed no splitting. All overlayer features were streaked in the [$\bar{1}$ 12] direction, which is consistent with a distribution of terrace widths and the clean surface LEED pattern.

IV. Theoretical Model: Details

We have calculated LEED beam intensities I(k) and integrated intensities using the theory described in Section II in a model appropriate to the O/stepped W(110) results discussed above. The Monte Carlo technique was used. All calculations were done at T = 0.04 eV on a single terrace of size Dx30, with periodic boundary conditions in the [$\bar{1}$ 11] direction. Our program was similar to one described by Landau[8]. The grand canonical ensemble was employed, and we used 6 randomly chosen initial configurations, calculated 240 configurations in each stream and kept 140 for averaging. The results reported are quite independent of the initial configuration - full or empty initial configurations changed none of the quantities significantly.

According to the general theory given above, there are three possibilities for the change in adsorption energy $\delta\varepsilon$ at the terrace edges: both $\delta\varepsilon>0$ (+ +), both $\delta\varepsilon<0$ (- -) and one of each (+ -). We set $|\delta\varepsilon|$ = 1eV in all cases. To obtain $\langle\rho(k)\rangle$ we Fourier transformed $\langle n_i\rangle$ directly. For (+ +) amd (- -) these averages were symmetrized after calculation. The integration region for Eq(4) was not reported by Engel et al.[2] For domain I (II) we assumed it to be an equal-sided parallelogram centered on the (1/2,1/2) ($(\overline{1/2},1/2)$) beam with an area of 4% of the (flat surface) Brillouin zone. In doing this h in Eq(1) was set equal to its maximum at the adlayer spot center. Since $\underline{k}\cdot\underline{g}$ was not reported, we set it equal to Π at the adlayer spot center and took $\underline{g} \parallel \underline{a}$ in the integration in Eq(4). These assumptions amount to dividing the [$\overline{1}$ 12] direction equally into regions centered on the peaks of h. The integral of h is equal to the integral of N_s over such a region, and we found the contribution of $|\langle\rho\rangle|^2$ to χ to be small. This confirms the general argument advanced in I (see Section II). $\langle|\rho|^2\rangle$ and $|\langle\rho\rangle|^2$ are similar smooth functions of θ so a change of integration region in χ should not alter our main conclusions, which are based only on trends in this quantity. However, the precise value of the coverage θ at the peak in χ_I might be altered slightly.

We note that a very interesting renormalization group treatment of finite size effects on overlayer thermodynamics has been presented by Berker and Ostlund[9]. This gives an alternate means of calculating some of the quantities determined with a Monte Carlo treatment here.

V. Theoretical Model: Results

First we discuss the integrated LEED intensity.

Results for χ_I vs. θ are shown in Fig. 4 for six cases: terrace width D=9 or 10 and terrace edge adsorption energy changes (+ +), (- -), and (+ -). We chose both an odd and even value of D near the observed average to check

for odd-even effects, which can be significant, as pointed out in Section II. The (- -) cases show no peak in Θ_I for $\theta < 0.5$. For D=9, (+ -) there is a peak slightly below $\theta = 0.5$. However Θ_I for D=10, (+ -) is increasing in this θ region and an average of the two shows little or no peak. This average is appropriate to the real surface, as remarked above. Clearly the (+ +) cases best reproduce the most striking feature in Θ_I, a maximum for $\theta < 0.5$. We regard this as the most convincing piece of evidence for weaker adsorption at the terrace edges. The apparent reason for it is also quite intuitive - excluding $\frac{2}{D}$ of the adsorption sites means that a complete (2x1) adlayer is formed at a lower value of θ. (This remark is elaborated on below, also see I). The experimental peak comes at a lower θ value than those in Fig. 4. In the context of our model, there are several possible reasons for this discrepancy. (i) The value of the Auger signal defining $\theta = 0.5$ was taken to be[2] that at which the LEED signal for the (2x1) domain on the flat surface was a maximum. This calibration procedure is somewhat sensitive to the defect concentration on the flat surface, and also to instrumental effects. (ii). The value of the LEED signal integration area on the stepped surface was not reported, and the peak in Θ_I may depend slightly on this quantity, as mentioned above. (iii). The stepped surface used had a distribution of step widths D, and the shift in the peak in Θ_I, depending mainly on $\frac{2}{D}$ (see below), is larger for smaller D values. (iv). The calculation presented here is for a single value of D only. (v). A final possibility is that the adsorption energy decreases at terrace edge sites and also at neighboring sites in the (1,0) direction. Despite these caveats, we feel the shift in the peak of Θ_I to a lower θ value in going from the flat to stepped surface is compelling evidence for the (+ +) case. This conclusion is strongly buttressed by the experimental results[2] for D=24. Here the peak is at a higher θ value ($\theta \cong 0.44$), but still less than 0.5, which is consistent with our interpretation.

At low coverage τ_I increases smoothly for either (+ +) case. For (+ -) one would expect it to grow smoothly ($\propto \theta^2$) for $\theta < 1/D$ as one row of adatoms forms at the attractive edge sites. For (- -), if we assume the edge sites fill up at equal rates as θ increases, there are two possibilities. For D=even, the edges cancel in phase, so τ_I will be quite small for $\theta < 2/D$. For D=odd, one expects $\tau_I \propto \theta^2$.

Actually, if one or both of the terrace sites were attractive, the low θ behavior could be more complicated[1]. Since the substrate structure is different at edge sites than elsewhere on the terrace, the adatom-adatom (AA) interactions may be different for these sites. Changes in the AA energies for the (+ -) or (- -) case would not affect the I domain LEED spots at low θ ($\leq \frac{1}{D}$ or $\leq \frac{2}{D}$, respectively). However it is possible for adlayer LEED spots not observed on the flat surface to occur, if the AA energies impose a new ordering along the terrace edges, or for the II domain LEED spot to be affected. See I for further discussion of this point. For this reason the low θ LEED behavior on stepped surfaces may be more complicated to interpret than what occurs for $\theta > \frac{2}{D}$.

Calculated values for τ_{II} are shown in Fig. 4. Note that for the (+ +) cases we recover what is observed, $\tau_I \cong \tau_{II}$ for low θ and $\tau_I > \tau_{II}$ at larger coverages. For the (- -) ((+ -)) case and $\theta < 2/D$ $(1/D)$ τ_{II} will be very small in our model since all the adatoms will be at terrace edge sites. (On the real surface it might be somewhat larger if there are defect sites we have not included here that can nucleate a II domain). Thus the (+ +) case again agrees with experiment and the others do not. Note that none of the cases show the observed minimum in τ_{II} near the maximum in τ_I. The reason for this may be due to the imposition of periodic boundary conditions in the [$\bar{1}$ 1 1] direction in our model. Different boundary conditions might cause II domains to nucleate more easily at low θ, only to disappear as θ increases and "crowding" in a long narrow terrace favors the I domain. However we have not checked this idea numerically.

Now we discuss LEED spot splitting. Although this may be a strong function of θ, experimental results were reported[2] at unrecorded θ values. We first confine our remarks to $\theta = 0.4$ since the remarks on splitting in Ref. 2 apparently refer to Fig. 2 of that work which is at this coverage. We found the I domain spot to be strongly split for all (+ -) and (- -) cases treated. If the spot center is at $\underline{k}_0$ and the maximum at $\underline{k}_1 = \underline{k}_0 + \frac{\pi}{a}\,\frac{1}{D}\,\hat{a}$ a measure of the intensity distribution in the split peaks is the ratio

$$R = I(\underline{k}_1) / I(\underline{k}_0) \tag{5}$$

For the (+ -) case we found R = 55 for D = 10, R = 11 for D = 9. For the (+ -) case, R = 69 for D = 10, R = 344 for D = 9. For the (+ +) case R = 191 for D = 9 while R = 0.7 for D = 10. However, the real stepped surface must have a distribution of even and odd D, so that the observed spot splitting is not inconsistent with the (+ +) value of R for D = 10. For the II domain, note that $\langle\rho(\underline{k})\rangle$ is the Fourier transform of $\langle n_i\rangle$. Using periodic boundary conditions this average is independent of the position of site i in the $[\bar{1}\ 11]$ direction. Hence $\langle\rho(\underline{k})\rangle = 0$ for the $(\overline{1/2},\ 1/2)$ beam and for any beam whose displacement is in the (1,1) reciprocal space direction from this point. So the contribution of $|\langle\rho(\underline{k})\rangle|^2$ to $I(\underline{k})$ (or I_{II}) is very small and one would expect no splitting of the II domain beam, as observed experimentally. On the real surface there are no periodic boundary conditions but a random distribution of terrace end locations in the $[\bar{1}\ 11]$ direction will have the same effect on $|\langle\rho\rangle|^2$.

As pointed out in I, the LEED spot splitting can be a strong function of θ. This general conclusion is born out by our numerical results. For the I domain, the ratio R in Eq(17) for (+ +), D = 10 is 0.95 at θ = .05, 0.67 for θ = 0.4, and 1.11 for θ = .55. For D = 9, R = 0.91 for θ = 0.03, 191 for θ = 0.41, 1577 for θ = .45, and 6 for θ = 0.63.

VI. Prospects for Further Work

We have considered the general theory of LEED scattering from certain types of overlayers on stepped surfaces including the effects of disorder in the overlayer for the first time. By comparison with experimental results of O on a stepped W(110) surface, we have demonstrated the adsorption at terrace edge sites on this particular surface is less strong than elsewhere on the terrace. This conclusion rests most strongly on a single experimental fact: that the peak intensity for LEED scattering from the I domain (see Section V and Fig. 2) occurs at a coverage θ less than that on the flat surface. Referring to the discussion in I and Section V, it seems clear that the three possibilities for terrace edge site adsorption energy changes, (+ +), (+ -) and (- -) should be easily distinguishable by a simple comparison of experimental results on the stepped and flat surfaces. This indeed seems to be the case, and we hope to spell out the full details elsewhere. For present purposes we confine ourselves to the following remarks. (i). The conclusion of Section V regarding the behavior of $\cdot_I$ near its maximum can be obtained by a simple T = 0 calculation very similar to that reported in I. This is reasonable, since the statistical behavior near a complete overlayer should not be strongly influenced by entropic effects in a finite system of this kind. (ii). The three cases (+ +), (+ -) and (- -) <u>almost</u>, but not quite, correspond to $\cdot_I$ peaking at $\theta = 0.5-\frac{1}{D}$, $\theta = 0.5$, and $\theta = 0.5+\frac{1}{D}$ respectively. The "not quite" refers to odd-even effects (see the (+ -) cases in Fig. 4, for instance). However this problem can be overcome by considering $\langle|\rho|^2\rangle - |\langle\rho\rangle|^2$, a quantity which is experimentally accessible, as follows from Eq(5). (iii). For lattice gas models with even AA interactions only, this last conclusion also holds for T > 0 by an application of up-down symmetry in the corresponding Ising model. If odd interactions are important, as appears to be generally the case[10] for indirect interactions in chemisorption systems, up-down symmetry no longer obtains. However we expect the method will still go through

since the shift in θ dependence is really due to stearic effects, and so should have consequences only weakly dependent on interaction symmetry.

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Note added in proof

Recent work by Besocke and Wagner[11] lends support to our conclusions about the change in O binding energy on the stepped W(110) surface of ref. 2 (and Fig. 2). Ref. 11 examines the coadsorption of O_2 and N_2 on two stepped W(110) surfaces. One of these has step edges in the [$\bar{1}$ 10] direction, the other in the [001] direction. It is concluded that N_2 adsorbs dissociatively at terrace edge sites in either case. Coadsorption of O poisons the N_2 dissociation, more strongly in the [$\bar{1}$ 10] case than the [001] case. This implies that the O binding energy for the former, at edge sites on at least one side of the terrace, is larger than on flat W(110); and that the O binding energy is probably slightly larger in the latter case. The distance between W atoms along a step edge decreases progressively as one goes from the [$\bar{1}$ 10] to [001] to the present (close-pack direction) case. Hence a progressive decrease in O binding energy at the terrace edge sites presents a consistent trend.

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Figure Captions

1. Adatom-Adatom interaction energies for O/W(110) as determined by Ching et al[4]. Their values are E_1 = -0.072 eV, E_2 = +0.08 eV, E_3 = -0.049 eV.

2. The stepped W(110) surface used in Ref. 2. Large circles: W substrate atoms, Small circles: O adatoms. Dark circles illustrate overlayer domain I, cross-hatched circles domain II.

3. Experimental results[2] for integrated LEED intensities $\mathcal{A}$ as a function of coverage. Circles $\mathcal{A}_I$, crosses $\mathcal{A}_{II}$.

4. Monte Carlo results for the integreated LEED intensities $\mathcal{A}_I/N_s N^2$ (circles) and $\mathcal{A}_{II}/N_s N^2$ (crosses) for various terrace widths and terrace edge adsorption energy changes (see text). (a) 9(++), (b) 10(++), (c) 9(--), (d) 10(--), (e) 9(+-), (f) 10(+-).

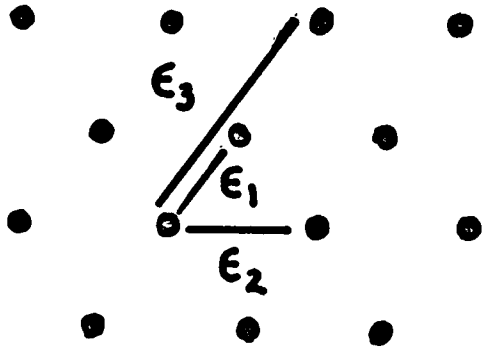

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Fig 1

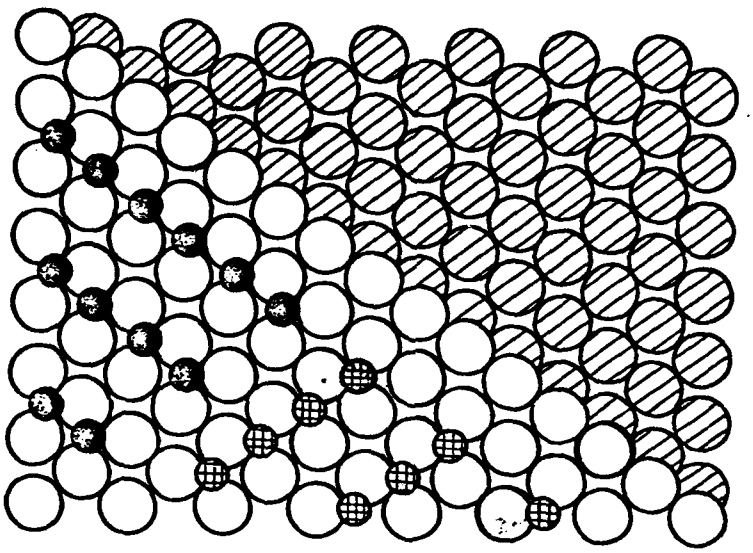

Fig 2
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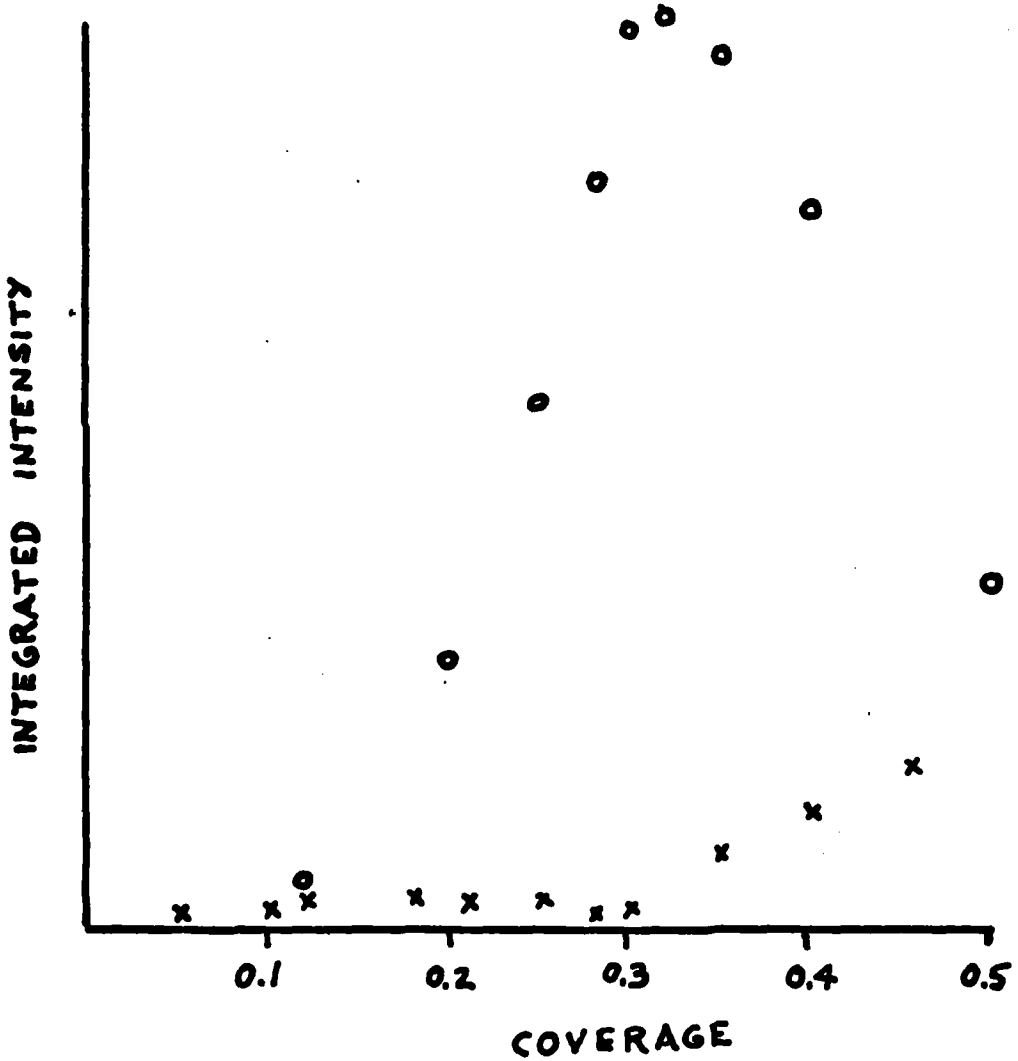
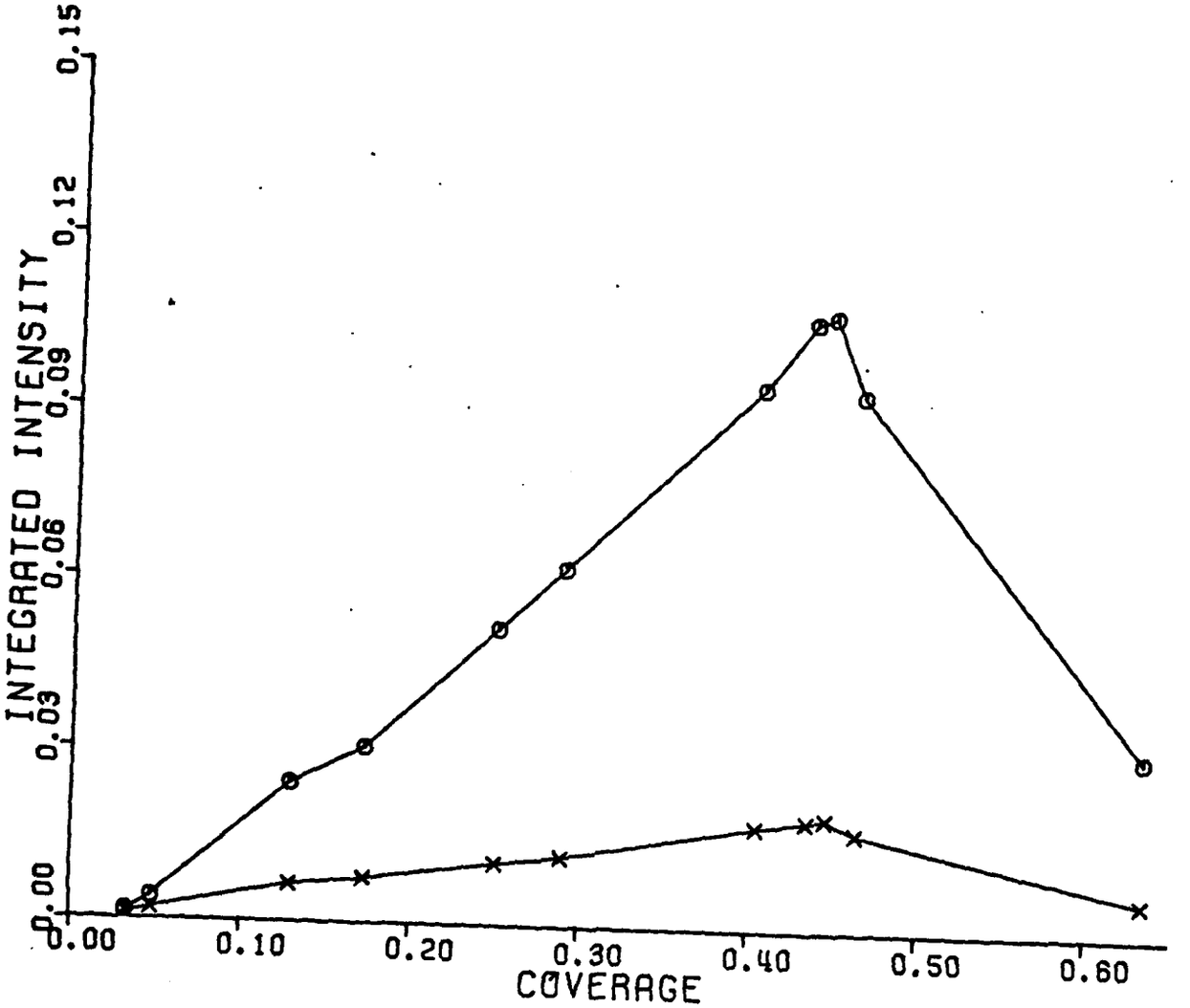
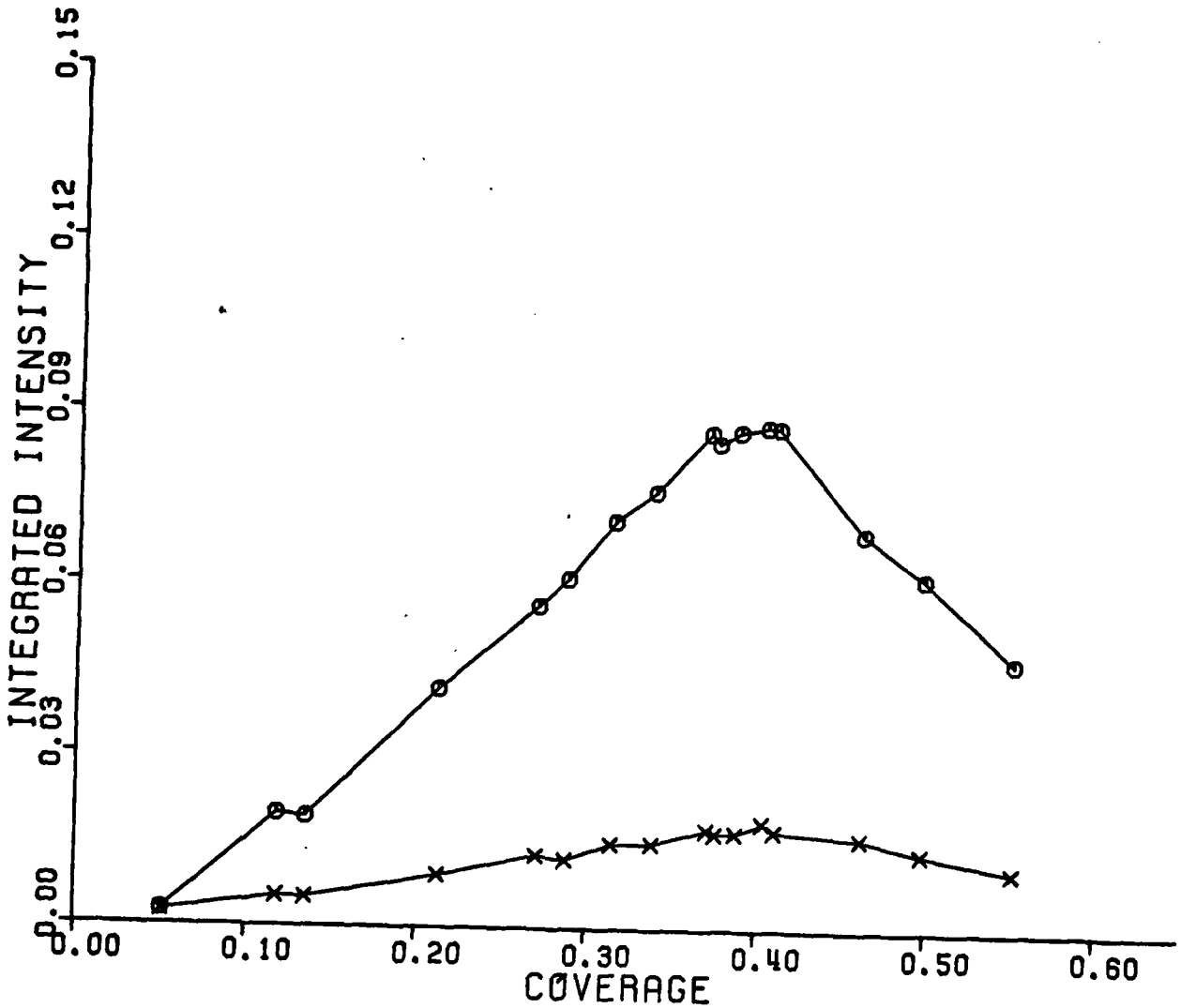


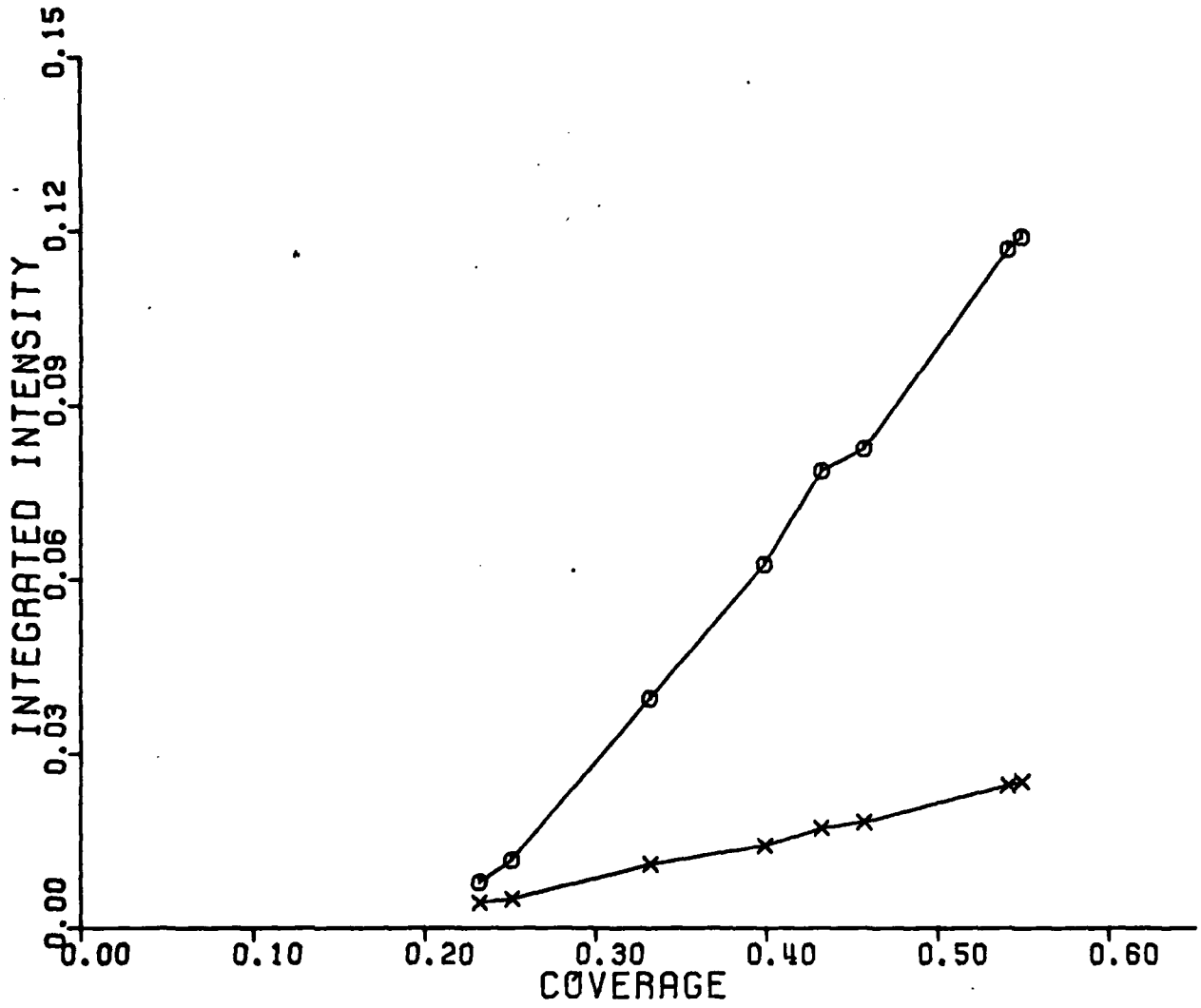
Kleban
Fig 3



Klebau
Fig 4/2
9-11



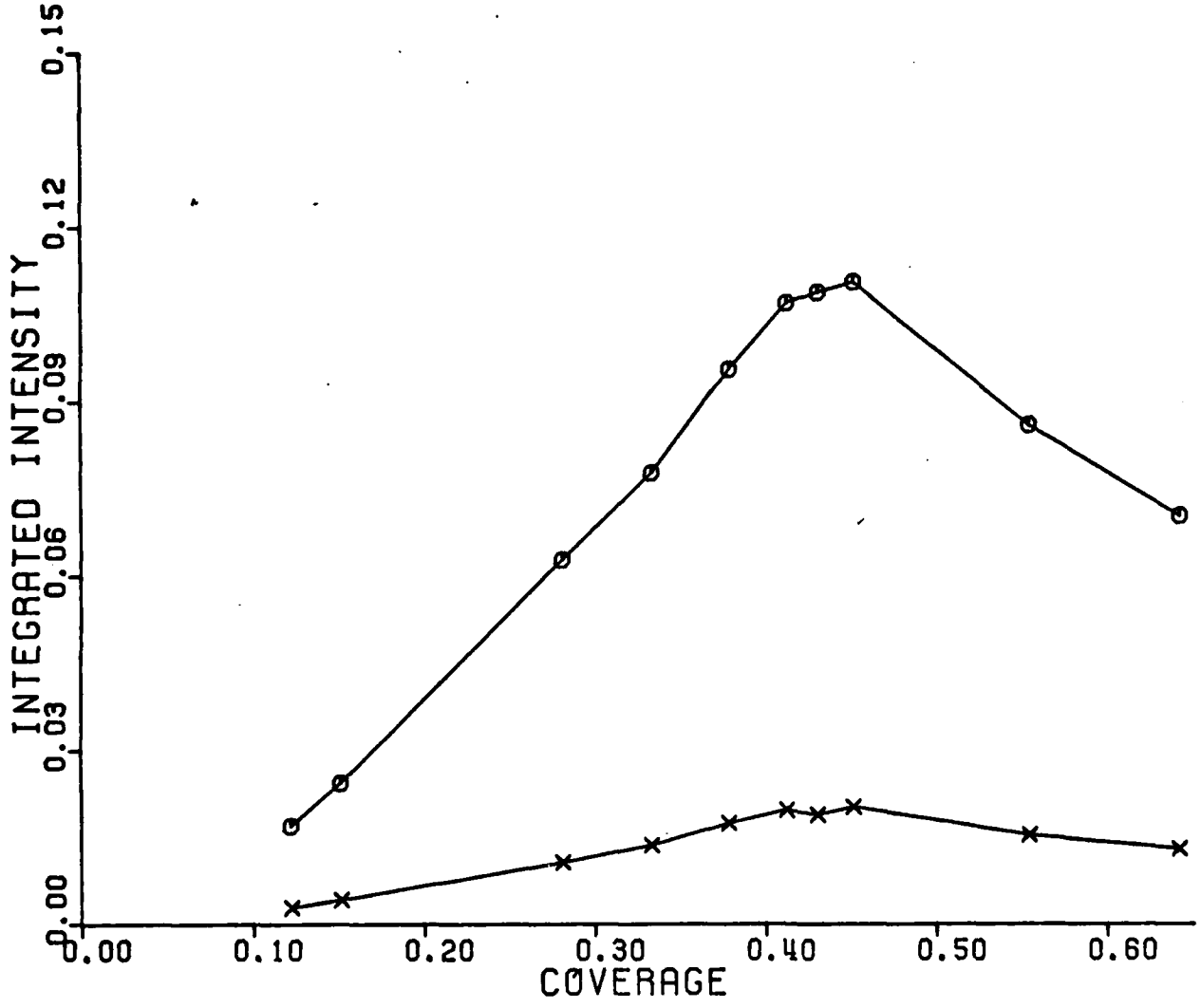
Kleban
Fig 4b
1044



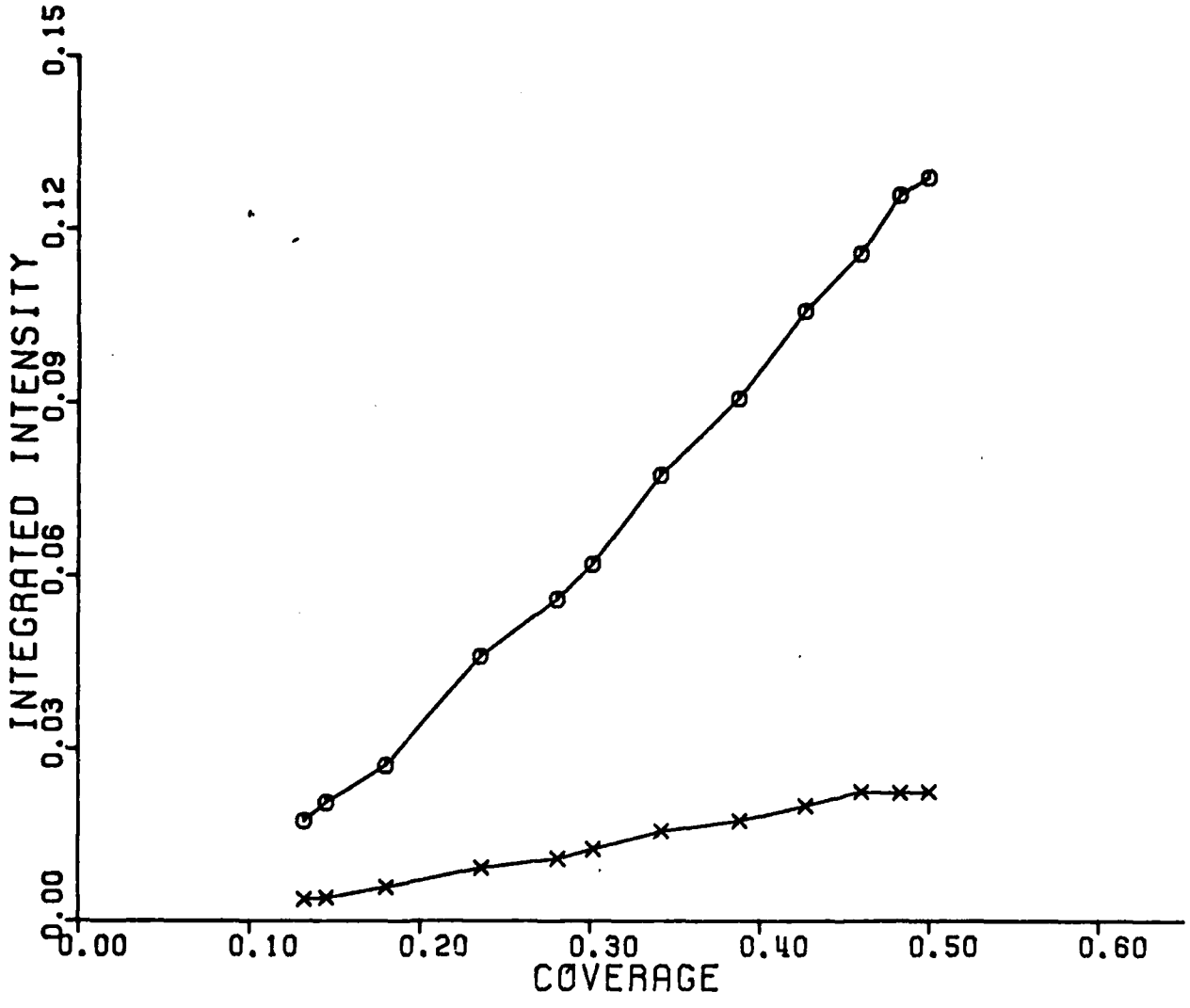
Ickbon
Fig 4c

20

INTEGRATED INTENSITY
0.00
0.03
0.06
0.09
0.12
0.15
0.00
0.10
0.20
0.30
0.40
0.50
0.60



Klebanoff
Figure
9:-


INTEGRATED INTENSITY
0.00
0.03
0.06
0.09
0.12
0.15
0.00
0.10
0.20
0.30
0.40
0.50
0.60
COVERAGE